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## Fluoride in dental erosion

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**Abstract:** Dental erosion develops through chronic exposure to extrinsic/intrinsic acids with a low pH. Enamel erosion is characterized by a centripetal dissolution leaving a small demineralized zone behind. In contrast, erosive demineralization in dentin is more complex as the acid-induced mineral dissolution leads to the exposure of collagenous organic matrix, which hampers ion diffusion and, thus, reduces further progression of the lesion. Topical fluoridation inducing the formation of a protective layer on dental hard tissue, which is composed of CaF<sub>2</sub> (in case of conventional fluorides like amine fluoride or sodium fluoride) or of metal-rich surface precipitates (in case of titanium tetrafluoride or tin-containing fluoride products), appears to be most effective on enamel. In dentin, the preventive effect of fluorides is highly dependent on the presence of the organic matrix. In situ studies have shown a higher protective potential of fluoride in enamel compared to dentin, probably as the organic matrix is affected by enzymatical and chemical degradation as well as by abrasive influences in the clinical situation. There is convincing evidence that fluoride, in general, can strengthen teeth against erosive acid damage, and high-concentration fluoride agents and/or frequent applications are considered potentially effective approaches in preventing dental erosion. The use of tin-containing fluoride products might provide the best approach for effective prevention of dental erosion. Further properly designed in situ or clinical studies are recommended in order to better understand the relative differences in performance of the various fluoride agents and formulations.

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## Fluoride in Dental Erosion

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**Short Title:** Fluorides and Erosion

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## Abstract

Dental erosion develops under the chronic exposure to extrinsic/intrinsic acids with a low pH. Enamel erosion is characterised by a centripetal dissolution leaving a small demineralised zone behind. In contrast, erosive demineralisation in dentine is more complex as the acid-induced mineral dissolution leads to the exposure of collagenous organic matrix, which hampers ion diffusion and, thus, reduces further progression of the lesion. Topical fluoridation inducing the formation of a protective layer on dental hard tissue, which is composed of  $\text{CaF}_2$  (in case of conventional fluorides like amine fluoride or sodium fluoride) or of metal-rich surface precipitates (in case of titanium tetrafluoride or tin-containing fluoride products), appears to be most effective on enamel. In dentine, the preventive effect of fluorides is highly dependent on the presence of the organic matrix. *In situ* studies showed a higher protective potential of fluoride in enamel compared to dentine, probably as the organic matrix is affected by enzymatical and chemical degradation as well as by abrasive influences in the clinical situation. There is convincing evidence that fluoride, in general, can strengthen tooth against erosive acid damage, and high concentration fluoride agents and/or frequent applications are considered potentially effective approaches to prevent dental erosion. The use of tin-containing fluoride products might provide the best approach for effective prevention of dental erosion. Further properly designed *in situ* or clinical studies are recommended in order to better understand the relative differences in performance of the various fluoride actives and formulations.

## Introduction

Dental erosion is defined as substance loss by exogenous or endogenous acids without bacterial involvement. The most important sources are dietary acids [1] and those originated from the stomach, like gastric acids from regurgitation and reflux disorders [2].

In contrast to initial caries, enamel erosion is predominantly a surface phenomenon with a centripetal bulk substance loss combined with a small partly demineralised surface layer with decreased microhardness (Figures 1 and 2). In dentine, the erosive demineralisation is mostly diffusion controlled, as the increasing exposure of organic matrix hampers ion diffusion and, thus, reduces further progression of dentine erosion (Figures 3 and 4) [3,4].

There is evidence that the prevalence of erosion is steadily increasing [5]. Preventive strategies in the management of dental erosion consider dietary counselling, stimulation of salivary flow, modification of erosive beverages, adequate oral hygiene measures and fluoride treatment as most relevant [6].

This chapter will give an overview about the current knowledge on the use of fluorides, including conventional and metal fluorides, for the prevention of erosive and combined erosive-abrasive dental loss. Due to the fact that the histology of enamel and dentine erosion is considerably different, this chapter will be divided in: 1) fluoride and enamel erosion; 2) fluoride and dentine erosion.

### Fluorides and enamel erosion

Extrinsic and/or intrinsic acids with low pH (pH 1.0-3.5) cause initially either the dissolution of the prism cores or of interprismatic areas, showing a honeycomb structure in prismatic enamel. In aprismatic enamel, the demineralisation is irregular, without a clear structural pattern. If the erosive challenge is ongoing, the dissolution process results in surface loss accompanied by a progressive softening of the surface. As the demineralised layer of eroded enamel is considerably small compared to the enamel loss, fluoride application predominately aims to prevent erosive tissue loss rather than to remineralise softened enamel.

Conventional fluorides whose beneficial effect against caries is well known [7] have been tested for prevention or control of dental erosion [8]. The potential of conventional fluorides, such as NaF and AmF, to prevent erosive demineralization is mainly related to the formation of a calcium fluoride ( $\text{CaF}_2$ )-layer [9,10] (Figure 5). This layer is assumed to behave as a physical barrier hampering the contact of the acid with the underlying enamel or to act as a mineral reservoir, which is attacked by the erosive challenge. Thereafter, calcium and fluoride released might increase the saturation level with respect to dental hard tissue in the liquid adjacent to the surface thus promoting remineralisation (Figures 6 and 7).

The formation of the  $\text{CaF}_2$ -like layer and its protective effect against demineralisation is highly dependent on the pH, the concentration of fluoride and the frequency of application. The deposition of calcium fluoride on the surface increases with increasing concentration and frequency of application and decreasing pH of the agent. Fluoride agents with a pH below 5 seem to induce a higher calcium fluoride deposition on dental surface than neutral ones [9].

Ganss *et al.* [10] evaluated the retention of calcium fluoride on human enamel under neutral and acidic conditions *in vitro* and *in situ*. Fluoride (10,000 ppm F, AmF) was applied once for 5 minutes and the enamel specimens were exposed to erosive demineralisation (3x 30s/day, 4 days *in vitro*/ 3x 2min/day, 7 days *in situ*) or neutral conditions (artificial saliva *in vitro*/ human saliva *in situ*). It was shown that more calcium fluoride was lost under erosive

compared to neutral conditions *in vitro*, while the intra-oral environment was considerably protective for  $\text{CaF}_2$ -like precipitates especially on enamel.

Although toothbrushing might affect the progression of eroded dental hard tissues adversely by removing the softened layer of enamel [11,12], it was shown that the use of fluoridated (NaF) toothpastes might diminish the abrasive effect to some extent [11,12,13]. However, as the overall protective effect of toothpastes with 1,100- 5,000  $\mu\text{g F/g}$  is limited [14,15], the use of high-concentrated fluoride varnishes (22,600  $\mu\text{g F/g}$ ) was anticipated to be more effective due to their capacity to adhere to the tooth surface and create a calcium fluoride reservoir [16,17]. Indeed, the application of NaF varnish (22,600  $\mu\text{g F/g}$ ) was effective in reducing enamel erosion for 30 minutes of acid exposure, but the protective effect declined thereafter [18,19]. However, as placebo varnishes also showed some protection against enamel erosion and combined erosion/abrasion, it is believed that the protective effect of fluoride varnishes is mainly related to the mechanical rather than to the chemical protection [20,21].

As the anti-erosive effect of conventional fluorides requires a very intensive fluoridation regime [22], recent studies have focused on fluoride compounds which might deliver a higher level of efficacy. In this context, compounds containing polyvalent metal ions such as stannous fluoride or titanium tetrafluoride were tested.

Several *in vitro* studies have shown an inhibitory effect of 0.4-10%  $\text{TiF}_4$  solution on dental erosion [23,24,25,26,27], which is attributed not only to the effect of fluoride, but mainly to the action of titanium [23,28]. Its protective effect is related to the formation of an acid-resistant surface coating, the increased fluoride uptake and the titanium incorporation in the hydroxyapatite lattice. The glaze-like surface layer observed after the application of  $\text{TiF}_4$  is assumed to be due to the formation of a new compound (hydrated hydrogen titanium phosphate) that might primarily act as a diffusion barrier [23,29,30,31,32] (Figures 8 and 9). The increased fluoride uptake found after application of  $\text{TiF}_4$  can be explained by the ability of the polyvalent metal ion to form strong fluoride complexes firmly bound to the apatite crystals [30,32].

Information regarding the efficacy of  $\text{TiF}_4$  under clinical conditions is scarce and contradictory, as only two *in situ* studies showed 1.6%  $\text{TiF}_4$  (0.5 M F) to be as effective as  $\text{SnF}_2$  or AmF in the prevention of erosion or combined erosion/abrasion [33,34], while other did not show any protective effect of 4%  $\text{TiF}_4$  [20,21,35]. The efficacy of  $\text{TiF}_4$  is highly dependent on the pH of the agent, since it was shown that enamel erosion can be significantly reduced by  $\text{TiF}_4$  (0.5 M F) at native pH (pH 1.2) but not at a pH buffered to 3.5 [36]. One study indicated that  $\text{TiF}_4$  applied in the form of a varnish might be of higher efficacy than as a solution [19]. However it should be consider that the low pH of  $\text{TiF}_4$  products does not allow self-application by the patient.

Tin-containing fluoride products have shown promising results in several studies [37,38,39 40,41]. The mode of action of tin-containing fluoride solutions is probably attributed to the formation of metal-rich surface precipitates [ $\text{Ca}(\text{SnF}_3)_2$ ,  $\text{SnOHPO}_4$ ,  $\text{Sn}_3\text{F}_3\text{PO}_4$ ], which were shown to be of high acid resistance [42] (Figures 9, 10 and 11). Further, tin may penetrate and become incorporated into the demineralized layer when high concentrated tin containing fluoride mouthrinses are used [38,43].

Ganss *et al.* [44] evaluated the relevance of cations in different fluoride compounds for their effectiveness as anti-erosive agents and showed that  $\text{SnCl}_2$  (800 ppm Sn), NaF (250 ppm F), AmF/ $\text{SnF}_2$  (250 ppm F/ 390 ppm Sn) and  $\text{SnF}_2$  (250 ppm F/ 809 ppm Sn) solutions could reduce enamel erosion. Treatment with solutions containing  $\text{SnF}_2$  was most effective. The combination of AmF/NaF/ $\text{SnCl}_2$  with high (2,800 ppm Sn/ 1,500 ppm F) and low (700 ppm Sn/ 1,500 ppm F) tin concentration reduced erosion by 90% and 70%, respectively [38,39].

Some possible side effects of high concentration tin containing mouthrinses may be dull feeling on the tooth surface, astringent sensation and tooth discolouration (1,900 ppm Sn) [45]. Therefore, tin-containing solutions of lower concentration (800 ppm Sn/ 500 ppm F) were tested *in vitro* and *in situ* [46,47]. Under severe erosive conditions, the  $\text{SnCl}_2$ /NaF/AmF exhibited a high potential to reduce enamel erosion (67% reduction), and showed no adverse side effects [47]. Besides mouthrinses, tin-containing fluoride toothpastes were tested in *in vitro* protocols and shown to perform significantly better under erosive challenges when

compared with NaF and MFP-containing toothpastes [41]. Further research should test specially formulated tin-containing fluoride products to minimize aesthetic negatives seen with high concentration tin-containing products, which may provide a highly effective means to help prevent dental erosion using a consumer-friendly approach.

### **Fluorides and dentine erosion**

The preventive effect of fluorides on dentine erosion is highly dependent on the presence of the organic matrix [48]. Initial studies showed that a very intensive fluoridation combining toothpaste (0.15% F, NaF), mouthrinse (0.025% F, AmF/NaF) and gel (1.25% F, AmF/NaF) application was most effective in the prevention of dentine erosion [22,49]. However, after enzymatic removal of the organic matrix fluoride was ineffective [3,50]. It was assumed that the demineralised organic dentine matrix has a buffering capacity sufficient to prevent further dentine demineralisation especially in the presence of high amounts of fluoride [3]. Moreover, the exposed organic matrix of etched dentine involves an increased surface area and increased diffusion pathways; enhancing the amount of structurally bound and KOH-soluble fluoride compared to sound dentine [51]. However, it remains unclear to which extent the organic material is retained under clinical conditions, when the collagen layer might be affected by enzymatical and chemical degradation as well as by abrasive influences [50,52]. From the clinical appearance of dentine erosive lesions it seems likely that the collagenous layer is at least partly removed. This hypothesis might also explain why fluorides such as NaF were less effective in dentine than in enamel under *in situ* conditions [22,10,38] but not in laboratory experiments [27,53].

The application of slightly acidic fluoride formulations such as NaF or AmF results in the formation of  $\text{CaF}_2$ -precipitates on both enamel and dentine (Figure 12), but the precipitates are less stable on dentine than on enamel under erosive conditions [10]. Although the preventive potential of NaF and AmF solution and dentifrice on dentine erosion and combined erosion/abrasion was shown in different *in situ* studies [22,34,54], information about the ideal fluoride concentration and frequency of application is scarce. Also, the



resistance of dentinal  $\text{CaF}_2$  precipitates against abrasion was not assessed directly so far; only *in situ* study indicated that the protective potential of AmF against erosion is not affected by additional brushing treatment [34].

Considering the severe and chronic acid exposure in patients suffering from dental erosion, the effect of  $\text{CaF}_2$ -precipitates is probably limited over time [10] and fluoride compounds with a distinct potential to resist an erosive challenge are required.

Titanium tetrafluoride was shown to induce some coating on dentine surfaces, which partly covered dentinal tubules [55] (Figure 13). However, its protective potential did not exceed the efficacy of NaF or AmF [27,34,56], and the low pH required for the efficacy of the agents do not allow for a clinical application so far [57].

Tin-containing fluoride solutions have been demonstrated to exhibit promising anti-erosive effects not only on enamel but also on dentine [38,44,46]. The suggested mechanism of action is related to the incorporation of tin in mineralised dentine when the organic matrix is allowed to develop and to surface precipitation when the organic matrix is enzymatically removed [58]. In case that the organic matrix is preserved, phosphorus, phosphorylated phosphoprotein or phosphophoryn might attract the tin-ion, which is then retained in the organic matrix to some extent but accumulates also in the underlying mineralised tissue. In case that the organic matrix is removed, tin reacts with the mineral by forming different salts, e.g.  $\text{Sn}(\text{OH})_2$ ,  $\text{Sn}_2(\text{PO}_4)\text{OH}$ ,  $\text{Ca}(\text{SnF}_3)$ ,  $\text{Sn}_3\text{F}_3\text{PO}_4$ ,  $\text{Sn}_2(\text{OH})\text{PO}_4$ ,  $\text{Sn}_3\text{F}_3\text{PO}_4$  or  $\text{SnHPO}_4$  [58]. Recent *in situ* studies demonstrated that mouthrinses containing AmF/NaF/ $\text{SnCl}_2$  (500 ppm F, 800 ppm Sn) reduced dentine erosion by 50% and were significantly more effective than a NaF-containing mouthrinse (500 ppm F) [38,47].

Comparing the protective effect of different fluoride compounds on dentine erosion, Ganss *et al.* [48] showed that solutions containing AmF and/or  $\text{SnF}_2$  performed only slightly better than solutions containing NaF and/or AmF in the presence of the organic matrix. However, continuous removal of the organic matrix influenced the efficacy of the fluoride compounds distinctly and demonstrated a significantly better preventive effect of the  $\text{SnF}_2$  and AmF/ $\text{SnF}_2$ -containing solutions compared to all other solutions.

## CONCLUDING REMARKS

Conventional fluorides with a known anti-cariogenic potential offer some, but limited protection against erosion as the  $\text{CaF}_2$  precipitates formed on the surface are readily soluble in acids. Metal-containing fluoride compounds showed promising results in prevention of erosion, but might involve some adverse side effects due to the very low pH (in case of titanium tetrafluoride) and the potential to cause slight discoloration, dull feeling on the tooth surface and astringent sensation (in case of high concentrated tin containing fluoride solutions).

There is convincing evidence that fluoride, in general, can strengthen enamel against erosive acid damage, high concentration fluoride agents and/or frequent applications are considered potentially effective approaches to prevent dental erosion. However, fluorides might be more effective in enamel than in dentine, as the organic matrix influencing the efficacy of fluorides might to some extent be affected by enzymatical and chemical degradation as well as by mechanical abrasion. The use of tin-containing fluoride products might provide the best approach for effective prevention of dental erosion.

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